

Claims

1. A method for producing powdered metal catalyst for use in the production of carbon nanostructures, which method comprises:

mixing a) one or more metal compounds selected from the group consisting of metal carbonates, metal nitrates, and metal hydroxides, wherein at least one of the metals is a Groups VIII metal, with b) one or more dispersing agents characterized as: i) being substantially inert with respect to reaction with the carbon-containing gas at temperatures up to at least about 750°C; (ii) being substantially inert with respect to chemical interaction with the catalytic metals at temperatures up to at least about 750°C; (iii) not having a deleterious effect on the catalytic activity of the catalytic metals; and (iv) capable of maintaining their physical integrity at temperatures up to at least about 750°C;

calcining the resulting mixture at a temperature from about 200°C to about 400°C for an effective amount of time to convert at least the metal compound to its respective oxide;

milling the calcined mixture for an effective amount of time to decrease the particles comprising the mixture to a predetermined size;

treating the milled, calcined mixture of particles with hydrogen for an effective amount of time and temperature to chemically reduce at least a portion of the catalytic metal oxides to the metallic state.

2. The method of claim 1 wherein the amount of dispersing agent used is from about 1 to 50 wt.%, based on the total amount of catalytic metal compound and dispersing agent.
3. The method of claim 2 wherein the amount of dispersing agent used is from about 5 to 25 wt.%
4. The method of claim 3 wherein the amount of dispersing agent used is from about 5 to about 10 wt.%.

- 5 The method of claim 1 wherein the dispersing agent is selected from the group consisting of alkaline halides, alkaline-earth halides, and metal oxides.
6. The method of claim 5 wherein the dispersing agent is an alkaline halide selected from the group consisting of sodium fluoride, sodium chloride, sodium bromide, potassium fluoride, potassium chloride, potassium bromide, lithium fluoride, and rubidium fluoride.
7. The method of claim 6 wherein the dispersing agent is sodium chloride.
8. The method of claim 5 wherein the dispersing agent is an alkaline-earth halide selected from the group consisting of calcium fluoride, calcium chloride, calcium bromide, magnesium fluoride, magnesium chloride, magnesium bromide, barium fluoride, barium chloride, barium bromide, strontium fluoride, strontium chloride and strontium bromide; preferred are calcium chloride and magnesium chloride, and more preferred is calcium chloride.
9. The method of claim 5 wherein the dispersing agent is a metal oxide selected from the group consisting of magnesia, silica, alumina, titania, tungsten oxide, tantalum oxide, molybdenum oxide, lanthanum oxide, tellurium oxide, chromium oxide, niobium oxide and zirconium oxide.
10. The method of claim 1 wherein the predetermined size is about 2.5 nm to about 100 nm.
11. The method of claim 1 wherein the catalytic metal is a bimetallic comprised of iron and nickel.
12. The method of claim 1 wherein the catalytic metal is a multimetallic comprised of at least one Group VIII metal and at least one Group IB metal.
13. The method of claim 12 wherein the catalytic metal is a bimetallic comprised of iron and copper.
14. A method for producing powdered metal catalyst for use in the production of carbon nanostructures, which method comprises:

calcining one or more metal compounds selected from the group consisting of metal carbonates, metal nitrates, and metal hydroxides, wherein at least one of the metals is a Groups VIII metal at a temperature from about 200°C to about 400°C for an effective amount of time to convert at least the metal compound to its respective oxide;

adding an effective amount of dispersing agent to the calcined metal compound, which dispersing agent is characterized as: i) being substantially inert with respect to reaction with the carbon-containing gas at temperatures up to at least about 750°C; (ii) being substantially inert with respect to chemical interaction with the catalytic metals at temperatures up to at least about 750°C; (iii) not having a deleterious effect on the catalytic activity of the catalytic metals; and (iv) maintaining their physical integrity at temperatures up to at least about 750°C;

milling the calcined metal compound and dispersing agent for an effective amount of time to decrease the particles comprising the mixture to a predetermined size;

chemically reducing the milled mixture of particles with hydrogen for an effective amount of time and temperature to reduce at least a portion of the catalytic metal oxides to the metallic state.

15. The method of claim 14 wherein the amount of dispersing agent used is from about 1 to 50 wt.%, based on the total amount of catalytic metal precursor and dispersing agent.

16. The method of claim 15 wherein the amount of dispersing agent used is from about 5 to 25 wt.%

17. The method of claim 16 wherein the amount of dispersing agent used is from about 5 to about 10 wt.%.

18. The method of claim 14 wherein the dispersing agent is selected from the group consisting of alkaline halides, alkaline-earth halides, and metal oxides.

19. The method of claim 18 wherein the dispersing agent is an alkaline halide selected from the group consisting of sodium fluoride, sodium chloride, sodium bromide,

potassium fluoride, potassium chloride, potassium bromide, lithium fluoride, and rubidium fluoride.

20. The method of claim 19 wherein the dispersing agent is sodium chloride.
21. The method of claim 18 wherein the dispersing agent is an alkaline-earth halide selected from the group consisting of calcium fluoride, calcium chloride, calcium bromide, magnesium fluoride, magnesium chloride, magnesium bromide, barium fluoride, barium chloride, barium bromide, strontium fluoride, strontium chloride and strontium bromide; preferred are calcium chloride and magnesium chloride, and more preferred is calcium chloride.
22. The method of claim 19 wherein the dispersing agent is a metal oxide selected from the group consisting of magnesia, silica, alumina, titania, tungsten oxide, tantalum oxide, molybdenum oxide, lanthanum oxide, tellurium oxide, chromium oxide, niobium oxide and zirconium oxide.
23. The method of claim 14 wherein the predetermined size is about 2.5 nm to about 100 nm.
24. The method of claim 14 wherein the catalytic metal is a bimetallic comprised of iron and nickel.
25. The method of claim 14 wherein the catalytic metal is a multimetallic comprised of at least one Group VIII metal and at least one Group IB metal.
26. The method of claim 14 wherein the catalytic metal is a bimetallic comprised of iron and nickel.
27. A method for producing a carbon nanostructure from a powdered metal catalyst, which method comprises:

mixing a) one or more metal compounds selected from the group consisting of metal carbonates, metal nitrates, and metal hydroxides, wherein at least one of the metals is a Groups VIII metal, with b) one or more dispersing agents characterized as: i) being

substantially inert with respect to reaction with the carbon-containing gas at temperatures up to at least about 750°C; (ii) being substantially inert with respect to chemical interaction with the catalytic metals at temperatures up to at least about 750°C; (iii) not having a deleterious effect on the catalytic activity of the catalytic metals; and (iv) capable of maintaining their physical integrity at temperatures up to at least about 750°C;

calcining the resulting mixture at a temperature from about 200°C to about 400°C for an effective amount of time to convert at least the metal compound to its respective oxide;

milling the calcined mixture for an effective amount of time to decrease the particles comprising the mixture to a predetermined size;

treating the milled, calcined mixture of particles with hydrogen for an effective amount of time and temperature to chemically reduce at least a portion of the catalytic metal oxides to the metallic state; and

decomposing a carbon-containing compound having up to about 8 carbon atoms in the presence of at least a portion of the reduced milled, calcined mixture of catalytic metal particles and dispersing agent at a temperature from about 450°C to about 800°C.

28. The method of claim 27 wherein the amount of dispersing agent used is from about 1 to 50 wt.%, based on the total amount of catalytic metal compound and dispersing agent.

29. The method of claim 28 wherein the amount of dispersing agent used is from about 5 to 25 wt.%

30. The method of claim 29 wherein the amount of dispersing agent used is from about 5 to about 10 wt.%.

31. The method of claim 27 wherein the dispersing agent is selected from the group consisting of alkaline halides, alkaline-earth halides, and metal oxides.

32. The method of claim 31 wherein the dispersing agent is an alkaline halide selected from the group consisting of sodium fluoride, sodium chloride, sodium bromide,

potassium fluoride, potassium chloride, potassium bromide, lithium fluoride, and rubidium fluoride.

33. The method of claim 32 wherein the dispersing agent is sodium chloride.
34. The method of claim 31 wherein the dispersing agent is an alkaline-earth halide selected from the group consisting of calcium fluoride, calcium chloride, calcium bromide, magnesium fluoride, magnesium chloride, magnesium bromide, barium fluoride, barium chloride, barium bromide, strontium fluoride, strontium chloride and strontium bromide; preferred are calcium chloride and magnesium chloride, and more preferred is calcium chloride.
35. The method of claim 31 wherein the dispersing agent is a metal oxide selected from the group consisting of magnesia, silica, alumina, titania, tungsten oxide, tantalum oxide, molybdenum oxide, lanthanum oxide, tellurium oxide, chromium oxide, niobium oxide and zirconium oxide.
36. The method of claim 27 wherein the predetermined size is about 2.5 nm to about 100 nm.
37. The method of claim 27 wherein the catalytic metal is a bimetallic comprised of iron and nickel.
38. The method of claim 27 wherein the catalytic metal is a multimetallic comprised of at least one Group VIII metal and at least one Group IB metal.
39. The method of claim 38 wherein the catalytic metal is a bimetallic comprised of iron and copper.
40. The method of claim 37 wherein the ratio of iron to nickel is from about 1:9 to about 9:1.

41. The method of claim 40 wherein the ratio of iron to nickel is from about 3:7 to about 7:3.
42. The method of claim 40 wherein the ratio of CO to H₂ is from about 95:5 to about 5:95.
43. The method of claim 42 wherein the ratio of CO to H₂ is from about 80:20 to about 20:80.
44. The method of claim 40 wherein the ratio of CO to H₂ is from about 80:20 to about 20:80.
45. The method of claim 14 wherein the particle size of the catalytic metal powder is from about 0.5 nanometer to about 5 micrometer.
46. The method of claim 45 wherein the particle size of the bimetallic powder is from about 2.5 nanometer to about 1 micrometer.
47. The method of claim 46 wherein the ratio of hydrogen to helium is about 4 to 1.
48. The method of claim 27 wherein the dispersing agent is removed from the resulting carbon nanofibers.
49. The method of claim 48 wherein the dispersing agent is removed from the resulting carbon nanofibers by dissolving the dispersing agent in a suitable solvent selected from the group consisting of water, dilute acid, or with a dilute alkali solution.
50. The method of claim 14 that includes a step of decomposing a carbon-containing compound having up to about 8 carbon atoms in the presence of at least a portion of the milled and reduced mixture of catalytic metal particles and dispersing agent at a temperature from about 450°C to about 800°C.